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(71) 出願人 000003182

株式会社トクヤマ

山口県徳山市御影町1番1号

(72) 発明者 平山 浩喜

山口県徳山市御影町1番1号 株式会社トクヤマ内

(72) 発明者 坂田 勘治

山口県徳山市御影町1番1号 株式会社トクヤマ内

(54) 【発明の名称】 イオン交換膜およびその用途

(57) 【要約】

【課題】拡散透析用隔膜として十分な機械的強度を有し、酸やアルカリの透過速度に優れるイオン交換膜を開発すること。

【解決手段】ポリオレフィン等の熱可塑性樹脂製多孔質膜を母材とし、その空隙部にイオン交換樹脂が充填されてなるイオン交換膜であって、膜厚が10～150 $\mu$ mであり、25℃における水の透水性が5 $\times$ 10<sup>-8</sup> m<sup>3</sup>/h/100kPa以下であることを特徴とするイオン交換膜。

## 【特許請求の範囲】

【請求項1】熱可塑性樹脂製多孔質膜を母材とし、その空隙部にイオン交換樹脂が充填されてなるイオン交換膜であって、膜厚が $10 \sim 150 \mu\text{m}$ であり、 $25^\circ\text{C}$ における水の透水性が $5 \times 10^{-8} \text{ m}^3/\text{h}/100 \text{ kPa}$ 以下であることを特徴とするイオン交換膜。

【請求項2】請求項1記載のイオン交換膜からなる拡散透析用隔膜。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、透析用隔膜、電池用隔膜、センサー等に使用されるイオン交換膜、特に拡散透析用隔膜として好適に使用されるイオン交換膜に関する。

## 【0002】

【従来の技術】イオン交換膜は、透析用隔膜、電池用隔膜等として汎用的に使用されている。このうち、イオン交換膜を用いた拡散透析は、濃度差による酸やアルカリの拡散現象を利用してこれらを分離回収する、エネルギー消費の少ない経済的な分離技術である。従って、近年、産業廃棄物として排出量が増加している廃酸や廃アルカリの回収技術として、該拡散透析を適用することが、環境保全、資源の有効活用等の観点から重要性を増している。

【0003】ところで、こうした拡散透析等の透析用隔膜に利用されるイオン交換膜は、機械的強度や耐薬品性に優れていることが望ましく、このため、熱可塑性樹脂製多孔質膜を母材とし、その空隙部にイオン交換樹脂を充填した膜が好適に使用されている。そして、こうした熱可塑性樹脂製多孔質膜を母材とするイオン交換膜は、例えば、イオン交換基の導入に適した官能基を有するモノマー、架橋剤および重合触媒からなる単量体組成物を、該熱可塑性樹脂製多孔質膜に含浸させ重合した後、イオン交換基を導入するという方法や、イオン交換樹脂を溶剤に溶解させた溶液を該熱可塑性樹脂製多孔質膜に含浸させ溶剤を除去させる方法等により一般的に製造されている（特開平6-329815号公報、特開平1-22932号公報等）。

## 【0004】

【発明が解決しようとする課題】ところが、上記のような方法により得られるイオン交換膜は、透水性を今一步十分に小さくできない問題があった。即ち、上記イオン交換膜は、熱可塑性樹脂製多孔質膜に含浸させるイオン交換樹脂溶液や単量体組成物が、該母材の空隙部の微細部まで十分に侵入し難く、さらに、イオン交換樹脂溶液を含浸させる方法にあつては含浸後に溶剤が除去されるため体積変化も生じてしまい、該母材の空隙部の微細部まで高密度にイオン交換樹脂が充填され難いものであった。従って、このようなイオン交換膜では、上記イオン交換樹脂が密に充填されていない微細空隙が若干残存してし

まい、これにより上記の如く膜の透水性を今一步十分に小さくできなかった。

【0005】そうして、このようなイオン交換膜を透析用隔膜として用いた場合には、透析中に、透析室側から希釈室側に向かって膜中をかなりの水が透過し、この流れにより、原料室側から透析室に浸透する酸やアルカリの浸透流が妨げられ、酸やアルカリの透過速度が低下してしまう問題が生じていた。特に、この透過速度の低下は、酸やアルカリの浸透が拡散現象のみにより行われる拡散透析の場合には顕著であった。

【0006】また、透析中の装置の運転環境の変動により、原料室液と透析室液との間に圧力差が生じた場合などには、上記濃縮室側から希釈室側への水の透過がさらに強まったり、或いは希釈室側から濃縮室側への水の強い透過が生じたりして、前者の場合には、上記原料室側から透析室側への酸やアルカリの透過速度がさらに低下し、後者の場合には、この水の浸透に伴って原料室中の他の不純物イオン（例えば、陰イオン交換膜を用いての酸の回収であれば金属イオン、陽イオン交換膜を用いての水酸化ナトリウムの回収であれば、多価金属イオン）が透析室に透過してしまう問題も生じていた。

【0007】以上から、十分な熱可塑性樹脂性多孔質膜を母材とし機械的強度に優れるイオン交換膜において、透水性が極めて小さく、拡散透析用隔膜として用いた場合に優れた酸またはアルカリの透過速度で透析が行えるイオン交換膜を開発することが望まれていた。

## 【0008】

【課題を解決するための手段】本発明者等は、上記課題に鑑み鋭意研究を行ってきた。その結果、熱可塑性樹脂製を母材とし、透水性が極めて小さいイオン交換膜を開発することに成功し、本発明を提案するに至った。

【0009】即ち、本発明は、熱可塑性樹脂製多孔質膜を母材とし、その空隙部にイオン交換樹脂が充填されてなるイオン交換膜であって、膜厚が $10 \sim 150 \mu\text{m}$ であり、 $25^\circ\text{C}$ における水の透水性が $5 \times 10^{-8} \text{ m}^3/\text{h}/100 \text{ kPa}$ 以下であることを特徴とするイオン交換膜である。

【0010】また、本発明は、上記イオン交換膜からなる拡散透析用隔膜も提供する。

【0011】即ち、本発明の特徴は、熱可塑性樹脂製多孔質膜の該連通孔による空隙部に実質的に完全にイオン交換樹脂、特にいわゆる炭化水素系のイオン交換樹脂が充填されている点にある。かくして水和力の高い炭化水素系イオン交換樹脂が熱可塑性樹脂製多孔質膜中に分散した形態のイオン交換膜となり、該熱可塑性樹脂製多孔質膜へのイオン交換樹脂の充填性を高め、イオン交換容量や固定イオン濃度を調節することにより、本発明のイオン交換膜の透水性を所望の範囲に設定することができる。

【0012】ここで、熱可塑性樹脂は、例えば、ポリ塩

化ビニル、塩化ビニル-酢酸ビニル共重合体、塩化ビニル-塩化ビニリデン共重合体、塩化ビニル-オレフィン共重合体等の塩化ビニル系樹脂；ポリテトラフルオロエチレン、ポリトリフルオロエチレン、ポリクロロトリフルオロエチレン、ポリ（テトラフルオロエチレン-ヘキサフルオロプロピレン）、ポリ（テトラフルオロエチレン-ペルフルオロアルキルエーテル）等のフッ素系樹脂；ナイロン6、ナイロン66等のポリアミド樹脂等が制限なく使用される。機械的強度、化学的安定性、耐薬品性に極めていることから、ポリオレフィン樹脂を用いるのが特に好ましい。

【0013】ポリオレフィン樹脂としては、エチレン、プロピレン、1-ブテン、1-ペンテン、1-ヘキセン、3-メチル-1-ブテン、4-メチル-1-ペンテン、5-メチル-1-ヘプテン等の $\alpha$ -オレフィンの単独重合体または共重合体が挙げられる。このうち、本発明では、ポリエチレン、ポリプロピレンが好ましく、特にポリエチレンが好ましい。ポリオレフィン樹脂の重量平均分子量は、1万以上、好適に1万~50万が好ましい。

【0014】また、これらの熱可塑性樹脂製多孔質膜は、更に、ポリプロピレン繊維等など熱可塑性樹脂製繊維の布状物によるバックングを有していても良い。

【0015】上記熱可塑性樹脂製多孔質膜の孔の平均孔径は0.05~5.0 $\mu\text{m}$ 、好適には0.1~1.0 $\mu\text{m}$ であり、空隙率が30~95%、より好ましくは40~90%のものが好ましい。平均孔径が0.05 $\mu\text{m}$ 以下の場合には酸またはアルカリの透過速度が低下し、平均孔径が5.0 $\mu\text{m}$ 以上の場合には機械的強度が低くなるので好ましくない。また、空隙率が30%以下の場合には、酸またはアルカリの透過速度が低下し、空隙率が95%以上の場合には機械的強度が低くなるので好ましくない。

【0016】さらに、熱可塑性樹脂製多孔質膜は、酸またはアルカリの透過速度を高めるという観点及び支持膜として必要な機械的強度を付与するという観点から、通常、10~150 $\mu\text{m}$ の厚みを有するものが好ましく、より好ましくは20~120 $\mu\text{m}$ の厚みを有するものが望ましい。これらの熱可塑性樹脂製多孔質膜は、熱可塑性樹脂製フィルムを延伸法等により多孔化したものが使用される。

【0017】本発明のイオン交換膜は、上記熱可塑性樹脂製多孔質膜の空隙部にイオン交換樹脂が充填されている。イオン交換樹脂のイオン交換基としては、水溶液中で負または正の電荷となりうる官能基なら特に制限されるものではないが、具体的には、陽イオン交換基の場合には、スルホン酸基、カルボン酸基、ホスホン酸基等が挙げられ、このうちスルホン酸基が特に好ましい。また、陰イオン交換基の場合には、1~3級アミノ基、4級アンモニウム基、ピリジル基、イミダゾール基、4級

ピリジニウム基等が挙げられ、このうち4級ピリジニウム基が特に好ましい。

【0018】本発明のイオン交換膜は、上記の如く薄い熱可塑性樹脂製多孔質膜を母材として用いている薄い膜であるにも関わらず、透水性が極めて小さい。即ち、25℃における透水性が $5 \times 10^{-8} \text{ m}^3/\text{h}/100 \text{ kPa}$ 以下、好適には $0.1 \sim 2 \times 10^{-8} \text{ m}^3/\text{h}/100 \text{ kPa}$ である。また、膜厚は、上記母材の膜厚から、10~150 $\mu\text{m}$ の厚みを有しており、好ましくは20~120 $\mu\text{m}$ の厚みを有している。

【0019】本発明のイオン交換膜は、このように透水性が極めて小さいため、これを透析用隔膜、特に拡散透析用隔膜として用いた場合には、優れた透過速度で酸、アルカリの透析を行うことができる。なお、本発明において、イオン交換膜の透水性は、JIS K 3821に準拠した純水透水性試験装置を用いて測定される。

【0020】本発明のイオン交換膜は、0.1mol/L-硫酸水溶液中での含水率が30~200%、好適には40~150%の値であるのが、より十分な透過速度で酸やアルカリを透過させることができ好ましい。このような範囲の含水率は、多孔質膜の空隙部に存在するイオン交換樹脂の有するイオン交換基の種類、イオン交換容量及び架橋度等により制御することができる。

【0021】さらに、本発明のイオン交換膜は、イオン交換容量が0.2~5mmol/g以上、好適には0.5~3mmol/gであるのが好ましい。

【0022】上記性状にある本発明のイオン交換膜は、如何なる方法により製造しても良いが、一般には、以下の方法により製造される。即ち、イオン交換基が導入可能な官能基またはイオン交換基を有する単量体、架橋性単量体および重合開始剤からなる単量体組成物を熱可塑性樹脂製多孔質膜に、減圧脱気しながら含浸させた後、単量体組成物を重合し、必要に応じて陽イオン交換基を導入する方法が挙げられる。

【0023】この製造方法において、イオン交換基が導入可能な官能基を有する単量体またはイオン交換基を有する単量体としては、従来公知であるイオン交換樹脂の製造において用いられている炭化水素系単量体が特に限定されずに使用される。具体的には、陽イオン交換基が導入可能な官能基を有する単量体としては、スチレン、ビニルトルエン、ビニルキシレン、 $\alpha$ -メチルスチレン、ビニルナフタレン、 $\alpha$ -ハロゲン化スチレン類等が挙げられる。また、陽イオン交換基を有する単量体としては、 $\alpha$ -ハロゲン化ビニルスルホン酸、スチレンスルホン酸、ビニルスルホン酸等のスルホン酸系単量体、メタクリル酸、アクリル酸、無水マレイン酸等のカルボン酸系単量体、ビニルリン酸等のホスホン酸系単量体、それらの塩類およびエステル類等が用いられる。

【0024】一方、陰イオン交換基が導入可能な官能基を有する単量体としては、スチレン、ビニルトルエン、

クロロメチルスチレン、ビニルピリジン、ビニルイミダゾール、 $\alpha$ -メチルスチレン、ビニルナフタレン等が挙げられる。また、陰イオン交換基を有する単量体としては、ビニルベンジルトリメチルアミン、ビニルベンジルトリエチルアミン等のアミン系単量体、ビニルピリジン、ビニルイミダゾール等の含窒素複素環系単量体、それらの塩類およびエステル類等が用いられる。

【0025】また、架橋性単量体としては、特に制限されるものではないが、例えば、ジビニルベンゼン類、ジビニルスルホン、ブタジエン、クロロブレン、ジビニルビフェニル、トリビニルベンゼン類、ジビニルナフタリン、ジアリルアミン、ジビニルピリジン類等のジビニル化合物が用いられる。

【0026】本発明では、上記したイオン交換基が導入可能な官能基を有する単量体またはイオン交換基を有する単量体や架橋性単量体の他に、必要に応じてこれらの単量体と共重合可能な他の単量体や可塑剤類を添加しても良い。こうした他の単量体としては、例えば、スチレン、アクリロニトリル、メチルスチレン、アクロレイン、メチルビニルケトン、ビニルビフェニル等が用いられる。また、可塑剤類としては、ジブチルフタレート、ジオクチルフタレート、ジメチルイソフタレート、ジブチルアジペート、トリエチルシトレート、アセチルトリブチルシトレート、ジブチルセバケート等が用いられる。

【0027】次に、本発明における重合開始剤としては、従来公知のものが特に制限なく使用される。こうした重合開始剤の具体例としては、オクタノイルパーオキシド、ラウロイルパーオキシド、 $t$ -ブチルパーオキシ-2-エチルヘキサノエート、ベンゾイルパーオキシド、 $t$ -ブチルパーオキシイソブチレート、 $t$ -ブチルパーオキシラウレート、 $t$ -ヘキシルパーオキシベンゾエート、ジ- $t$ -ブチルパーオキシド等の有機過酸化物が用いられる。

【0028】本発明において、単量体組成物を構成する各成分の配合割合は、本発明の目的を達成するためには、一般には、イオン交換基が導入可能な官能基を有する単量体またはイオン交換基を有する単量体100重量部に対して、架橋性単量体を0.1~50重量部、好適には1~40重量部、これらの単量体と共重合可能な他の単量体を0~100重量部、可塑剤類を添加する場合は上記単量体に対して0~50重量部使用するのが好適である。また、重合開始剤は、イオン交換基が導入可能な官能基を有する単量体またはイオン交換基を有する単量体100重量部に対して、0.1~20重量部、好適には0.5~10重量部配合させるのが好ましい。

【0029】母材である熱可塑性樹脂製多孔質膜への上記単量体組成物の充填方法は、該多孔質膜の空孔の微細部まで密に単量体組成物が充填できる方法でなければならない。上記した単量体組成物を熱可塑性樹脂製多孔

質膜に、減圧脱気しながら含浸させる方法を採用するのが好適である。このように減圧下で脱気して含浸させれば、空隙部の微細部まで隙間なく単量体組成物を充填させることが可能になる。そして、かかる含浸後、単量体組成物を重合したイオン交換膜は、前記本願発明が特定するような透水性が極めて小さい性状の膜になる。

【0030】ここで、上記減圧脱気しながらの含浸処理は、具体的には、単量体組成物を熱可塑性樹脂製多孔質膜に減圧下で接触させ、圧力を大気圧に戻すことで行われる。例えば、熱可塑性樹脂製多孔質膜を容器に入れ、真空ポンプで減圧状態にした後、単量体混合物を大気圧に戻るまで容器に導入して浸漬させる方法、または、容器に入れた単量体混合物に熱可塑性樹脂製多孔質膜を浸漬し、真空ポンプで孔中の気体を減圧脱気した後大気圧に戻す方法等が挙げられる。減圧する時の減圧度は、7 kPa~作業温度下で単量体が沸騰するまでの圧力が好ましく、特に2 kPa~0.1 kPaの範囲から採択するのが好ましい。含浸時の温度は、20℃以下が一般的であり、含浸時間は、通常、5~60分の範囲で適宜採択すればよい。

【0031】単量体組成物を上記したように熱可塑性樹脂製多孔質膜に充填させたのち重合するには、一般にポリエステル等のフィルムに挟んで加圧下で常温から昇温する方法が好ましい。こうした重合条件は、関与する重合開始剤の種類、単量体組成物の組成等によって左右されるものであり、特に限定されるものではなく適宜選択すれば良い。

【0032】以上のように重合されて得られる膜状物は、必要に応じてこれを、公知の例えば、陽イオン交換膜であれば、スルホン化、クロルスルホン化、ホスホンウム化、加水分解等の処理、陰イオン交換膜であれば、アミノ化、アルキル化等の処理により所望のイオン交換基を導入して、イオン交換膜とすることができる。

【0033】

【発明の効果】本発明のイオン交換膜は、機械的強度や耐薬品性に優れ、熱可塑性樹脂製多孔質膜の空隙部に架橋したイオン交換樹脂が微細部まで隙間なく充填されていることから、膜厚が10~150  $\mu$ mの薄い膜であるにも関わらず、透水性が極めて小さい。そのため、電気透析や拡散透析等の透析用隔膜、特に拡散透析用隔膜として用いた場合、優れた透過速度で酸やアルカリを透過させることができ、効率的な透析を行うことができる。また、このように熱可塑性樹脂製多孔質膜の空隙部微細部までイオン交換樹脂が密に充填されているため、内部に残存する空隙を通じての、他の不純物イオンの透過がほとんど生じず、良好な選択透過性で酸やアルカリを透過させることができる。

【0034】さらには、透析中の運転環境の変動により、原料室液と透析室液との間に圧力差が生じた場合でも、膜の透水量に大きな変化が生じず、上記酸やアルカ

りの透過速度のさらなる低下や、他の不純物イオンの透析室への透過が強まることが防止される。

【0035】従って、かような性状を有する本発明のイオン交換膜は、上記拡散透析用隔膜として好適に使用できる。その場合、陰イオン交換膜を用いて透析する酸としては、硫酸、塩酸、硝酸、硝フッ酸、リン酸等が挙げられ、他方、陽イオン交換膜を用いて透析するアルカリとしては、水酸化ナトリウム、水酸化カリウム等が挙げられる。これらの酸やアルカリが含有される産業排水を被処理液とし、これらから酸やアルカリを回収する際に、適用するのが特に好ましい。また、本発明のイオン交換膜は、透水性が小さい性状を利用して、電気透析等のその他の透析用の隔膜やレドックスフロー電池等のセパレータ、イオンセンサー用の膜等の水溶液中のイオンを透過させるイオン交換膜の使用分野において、良好に用いることができる。

【0036】

【実施例】以下、本発明を更に詳細に説明するため実施例を挙げるが、本発明はこれらの実施例に限定されるものではない。

【0037】なお、実施例、比較例においてイオン交換膜の特性評価に用いたイオン交換容量、含水率、透水性、物質透過速度の測定方法を以下に説明する。

【0038】1) イオン交換容量および含水率  
イオン交換膜を1mol/L-HClに10時間以上浸漬する。

【0039】その後、陽イオン交換膜の場合には、1mol/L-NaClで水素イオン型をナトリウムイオン型に置換させ、遊離した水素イオンを電位差滴定装置 (COMTITE-900、平沼産業株式会社製) で定量した (Amol)。一方、陰イオン交換膜の場合には、1mol/L-NaNO<sub>3</sub>で塩素イオン型を硝酸イオン型に置換させ、遊離した塩素イオンを電位差滴定装置 (COMTITE-900、平沼産業株式会社製) で定量した (Amol)。

【0040】次に、同じイオン交換膜を1mol/L-HClに4時間以上浸漬し、イオン交換水で十分に水洗した後膜を取り出しティッシュペーパー等で表面の水分をふき取り湿潤時の重さ (Wg) を測定した。次に、膜を減圧乾燥機に入れ60℃で5時間乾燥させた。膜を取り出し乾燥時の重さ (Dg) を測定した。

【0041】イオン交換容量と含水率は次式により算出した。

【0042】イオン交換容量 =  $A \times 1000 / W$  [mmol/g-乾燥膜]

含水率 =  $100 \times (W - D) / D$  [%]

2) 透水性

JIS K 3821に準拠した純水透水性試験装置を用いた。測定に用いたイオン交換膜は25℃において含水状態で純水透水性試験装置に装着した。透水性は次式

により求めた。

【0043】 $C = Q25 / P$

C: 透水性 [m<sup>3</sup>/h/100kPa]

Q25: 25℃における水の透過流量 [m<sup>3</sup>/h]

P: 平均膜差圧 [kPa]

3) 酸、アルカリの透過速度

陰イオン交換膜では、陰イオン交換膜で区切られたアクリル樹脂製の二室セルを用い、一室 (原液室) に25℃の1mol/L-硫酸と0.5mol/L-硫酸マグネシウムを含む液を入れ、もう一室 (透析液室) には25℃のイオン交換水を入れた。攪拌子により両室を攪拌し一定時間後に透析液室の液を抜き取り、電位差滴定によって硫酸の透過量を、原子吸光光度計によって硫酸マグネシウムの透過量をそれぞれ測定した。

【0044】また、陽イオン交換膜では、上記方法において1mol/L-硫酸と0.5mol/L-硫酸マグネシウムを含む液を3mol/L-水酸化ナトリウムと0.5mol/L-水酸化アルミニウムを含む液に代えて同様な操作を行い、水酸化ナトリウムと水酸化アルミニウムの透過量を測定した。それぞれの物質の透過速度は次式により求めた。

【0045】 $U = A / (T \cdot S \cdot \Delta C)$

U: 酸またはアルカリの透過速度 [mol/Hr · m<sup>2</sup> · (mol/L)]

A: 酸またはアルカリの透過量 [mol]

T: 攪拌時間 [Hr]

S: 有効膜面積 [m<sup>2</sup>]

ΔC: 攪拌前後の両室の酸またはアルカリの対数平均濃度差 [mol/L]

実施例1~5

表1に示した組成表に従って、各種単量体等を混合して単量体組成物を得た。得られた単量体組成物400gを500mlのガラス容器に入れ、重量平均分子量10万のポリエチレン製多孔質膜 (A、B、C、D、各20cm×20cm) および重量平均分子量15万のポリプロピレン製多孔質膜 (E、20cm×20cm) を浸漬した。

【0046】次に、ガラス容器を真空ポンプで0.7kPaの圧力まで10分間減圧にして減圧脱気した後、常圧に戻して多孔質膜の空孔に単量体組成物を充填した。続いて、多孔質膜を単量体組成物中から取り出し、100μmのポリエステルフィルムを剥離材として多孔質膜の両側を被覆した後、0.4MPaの窒素加圧下、80℃で8時間加熱重合した。

【0047】得られた膜状物をヨウ化メチルとメタノールの1:4の混合物中に30℃で24時間浸漬し、ビリジニウム型陰イオン交換膜を得た。

【0048】これらのビリジニウム型陰イオン交換膜の膜厚、イオン交換容量、含水率、透水性、物質透過速度を測定した。これらの結果を表2に示した。

## 【0049】比較例1

実施例1において減圧脱気操作を行わなかった以外は実施例1と同じ操作を行いピリジニウム型陰イオン交換膜を得た。

【0050】このピリジニウム型陰イオン交換膜の膜厚、イオン交換容量、含水率、透水性、 $H_2SO_4$ 透過速度を測定した。この結果を表2に示した。

## 【0051】比較例2

市販されている陰イオン交換膜（市販品A；（株）トクヤマ製）を用い同様に膜厚、イオン交換容量、含水率、透水性、 $H_2SO_4$ 透過速度を測定した。その結果を表2に示した。

## 【0052】比較例3

ポリエチレン多孔質膜（A）を平均分子量20万のポリスチレンの10%ベンゼン溶液に5分間浸漬した。その後、液中からポリエチレン多孔質膜を取り出し、50℃で乾燥した。この操作を5回繰り返した後、80℃で2時間減圧乾燥し膜状物を得た。

【0053】得られた膜状物を2重量%の無水塩化スズを添加したクロロメチルメチルエーテルに浸漬し、35℃で4時間反応させた後、メチルアルコールで洗浄した。

【0054】次に、クロロメチル化した膜状物を30%トリメチルアミンとアセトンおよびイオン交換水の20:30:50の混合溶液に30℃で24時間反応させ、イオン交換基として第四級アンモニウム塩基を有する陰イオン交換膜を得た。

【0055】この陰イオン交換膜の膜厚、イオン交換容量、含水率、透水性、 $H_2SO_4$ 透過速度を測定した。その結果を表2に示した。

## 【0056】実施例6～10

表1に示した組成表に従って実施例1～5と同じ含浸お

よび重合操作を行ない、得られた膜状物を98%濃硫酸と純度90%以上のクロロスルホン酸の1:1の混合物中に40℃で45分間浸漬し、スルホン酸型陽イオン交換膜を得た。

【0057】これらのスルホン酸型陽イオン交換膜の膜厚、イオン交換容量、含水率、透水性、 $NaOH$ 透過速度を測定した。これらの結果を表3に示した。

## 【0058】比較例4

実施例6において減圧脱気操作を行わなかった以外は実施例6と同じ操作を行いスルホン酸型陽イオン交換膜を得た。

【0059】このスルホン酸型陽イオン交換膜の膜厚、イオン交換容量、含水率、透水性、 $NaOH$ 透過速度を測定した。この結果を表3に示した。

## 【0060】比較例5

市販されている陽イオン交換膜（市販品B；（株）トクヤマ製）を用い同様に膜厚、イオン交換容量、含水率、透水性、 $NaOH$ 透過速度を測定した。その結果を表3に示した。

## 【0061】比較例6

ポリエチレン多孔質膜（A）を平均分子量20万のポリスチレンの10%ベンゼン溶液に5分間浸漬した。その後、液中からポリエチレン多孔質膜を取り出し、50℃で乾燥した。この操作を5回繰り返した後、80℃で2時間減圧乾燥し膜状物を得た。

【0062】得られた膜状物を98%濃硫酸中に40℃で60分間浸漬し、スルホン酸型陽イオン交換膜を得た。このスルホン酸型陽イオン交換膜の膜厚、イオン交換容量、含水率、透水性、 $NaOH$ 透過速度を測定した。これらの結果を表3に示した。

## 【0063】

## 【表1】

表1

| 実施例No. | 多孔質膜 <sup>1)</sup> | 組成(重量比)          |                    |                   |                    |                  |
|--------|--------------------|------------------|--------------------|-------------------|--------------------|------------------|
|        |                    | St <sup>2)</sup> | 4-VP <sup>3)</sup> | DVB <sup>4)</sup> | ATBC <sup>5)</sup> | PO <sup>6)</sup> |
| 1      | A                  |                  | 80                 | 7                 | 5                  | 5                |
| 2      | B                  |                  | 80                 | 7                 | 5                  | 5                |
| 3      | C                  |                  | 80                 | 7                 | 5                  | 5                |
| 4      | D                  |                  | 80                 | 7                 | 5                  | 5                |
| 5      | E                  |                  | 80                 | 7                 | 5                  | 5                |
| 6      | A                  | 80               |                    | 7                 | 10                 | 5                |
| 7      | B                  | 80               |                    | 7                 | 10                 | 5                |
| 8      | C                  | 80               |                    | 7                 | 10                 | 5                |
| 9      | D                  | 80               |                    | 7                 | 10                 | 5                |
| 10     | E                  | 80               |                    | 7                 | 10                 | 5                |

1) 多孔質膜

A: ポリエチレン製、膜厚25 $\mu m$ 、空隙率46%、平均孔径0.5 $\mu m$   
 B: ポリエチレン製、膜厚50 $\mu m$ 、空隙率60%、平均孔径0.5 $\mu m$   
 C: ポリエチレン製、膜厚70 $\mu m$ 、空隙率80%、平均孔径0.5 $\mu m$   
 D: ポリエチレン製、膜厚100 $\mu m$ 、空隙率80%、平均孔径0.5 $\mu m$   
 E: ポリプロピレン製、膜厚50 $\mu m$ 、空隙率70%、平均孔径0.2 $\mu m$

2) スチレン

3) 4-ビニルピリジン

4) ジビニルベンゼン

5) アセチルクエン酸トリブチル

6) t-ブチルパーオキシエチルヘキサノエート

表2

| 実施例No. | 膜厚  | イオン<br>交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度                                   |                           |
|--------|-----|-------------|-----|----------------------|--|---------------------------|
|        |     |             |     |                      | H <sub>2</sub> SO <sub>4</sub><br>透過速度 | MgSO <sub>4</sub><br>透過速度 |
| 1      | 32  | 2.6         | 68  | 1.2                  | 26                                     | 0.091                     |
| 2      | 63  | 2.7         | 70  | 0.9                  | 22                                     | 0.083                     |
| 3      | 87  | 3.1         | 72  | 0.6                  | 18                                     | 0.076                     |
| 4      | 115 | 3.2         | 80  | 0.6                  | 15                                     | 0.066                     |
| 5      | 58  | 2.5         | 68  | 0.8                  | 20                                     | 0.078                     |
| 比較例1   | 30  | 1.6         | 55  | 29.2                 | 12                                     | 1.035                     |
| 比較例2   | 150 | 3.5         | 80  | 7.0                  | 6                                      | 0.101                     |
| 比較例3   | 29  | 0.2         | 30  | 82.4                 | 9                                      | 2.024                     |

膜厚[ $\mu\text{m}$ ]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

H<sub>2</sub>SO<sub>4</sub>透過速度[mol·Hr<sup>-1</sup>·m<sup>-2</sup>·(mol·L)<sup>-1</sup>]MgSO<sub>4</sub>透過速度[mol·Hr<sup>-1</sup>·m<sup>-2</sup>·(mol·L)<sup>-1</sup>]透水性[m<sup>3</sup>/Hr/100kPa]

選択透過性[ - ]

【0065】

【表3】

表3

| 実施例No. | 膜厚  | イオン<br>交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度         |                             |
|--------|-----|-------------|-----|----------------------|--------------|-----------------------------|
|        |     |             |     |                      | NaOH<br>透過速度 | Al(OH) <sub>3</sub><br>透過速度 |
| 6      | 35  | 2.7         | 59  | 1.3                  | 5.2          | 0.072                       |
| 7      | 62  | 2.6         | 58  | 0.8                  | 4.6          | 0.081                       |
| 8      | 88  | 3.0         | 69  | 0.6                  | 4.2          | 0.049                       |
| 9      | 114 | 3.1         | 72  | 0.4                  | 3.8          | 0.033                       |
| 10     | 59  | 2.6         | 62  | 0.8                  | 4.7          | 0.055                       |
| 比較例4   | 31  | 2.1         | 60  | 50.7                 | 3.3          | 0.986                       |
| 比較例5   | 180 | 2.5         | 51  | 8.8                  | 1.2          | 0.572                       |
| 比較例6   | 31  | 0.2         | 32  | 70.4                 | 3            | 0.802                       |

膜厚[ $\mu\text{m}$ ]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

NaOH透過速度[mol·Hr<sup>-1</sup>·m<sup>-2</sup>·(mol·L)<sup>-1</sup>]Al(OH)<sub>3</sub>透過速度[mol·Hr<sup>-1</sup>·m<sup>-2</sup>·(mol·L)<sup>-1</sup>]透水性[m<sup>3</sup>/Hr/100kPa]

選択透過性[ - ]

【手続補正書】

【提出日】平成10年7月1日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0012

【補正方法】変更

【補正内容】

【0012】ここで、熱可塑性樹脂は、例えば、ポリ塩

化ビニル、塩化ビニル-酢酸ビニル共重合体、塩化ビニル-塩化ビニリデン共重合体、塩化ビニル-オレフィン共重合体等の塩化ビニル系樹脂；ナイロン6、ナイロン66等のポリアミド樹脂等が制限なく使用される。機械的強度、化学的安定性、耐薬品性に極めていることから、ポリオレフィン樹脂を用いるのが特に好ましい。

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(72)Inventor : HIRAYAMA HIROKI  
SAKATA KANJI

## (54) ION EXCHANGE FILM AND ITS USE

## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ion exchange film having low water permeability, though it is thin, capable of carrying out dialysis at high permeation speed of an acid or alkali when used for diaphragm for diffusion and dialysis and useful for recovery, etc., of waste acids and waste alkalis by limiting film thickness and water permeability of the ion exchange film within a specific range.

SOLUTION: In this ion exchange film constituted so as to pack (B) an ion exchange resin in the space part of (A) a porous film made of a thermoplastic resin (e.g. a porous film with 10,000 to 500,000 weight average molecular weight having 0.05-5  $\mu$ m average diameter and 30-95% porosity) as a matrix, the film thickness is controlled to 10-150  $\mu$ m and water permeability at 25° C is controlled to  $5 \times 10^{-8}$  m<sup>3</sup>/h/100 kPa. The ion exchange film is obtained by impregnating, e.g. a monomer composition comprising a monomer having a functional group or ion exchange group capable of introducing ion exchange group and a crosslinkable monomer and a polymerization initiator into the component A while degassing under reduced pressure, polymerizing the monomer composition and as necessary, introducing an ion exchange group thereinto.

## LEGAL STATUS

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CLAIMS

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[Claim(s)]

[Claim 1] Ion exchange membrane which uses porous membrane made of thermoplastics as a base material, and it is the ion exchange membrane with which it comes to fill up the opening section ion exchange resin, and thickness is 10-150 micrometers, and is characterized by the water permeability of the water in 25 degrees C being  $h/100$  or less  $kPa \cdot cm^3 / (5 \times 10^{-8} m^3)$ .

[Claim 2] The diaphragm for diffusion dialyses which consists of ion exchange membrane according to claim 1.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ion exchange membrane used for the diaphragm for dialysis, the diaphragm for cells, a sensor, etc., especially the ion exchange membrane suitably used as a diaphragm for diffusion dialyses.

[0002]

[Description of the Prior Art] Ion exchange membrane is used general-purpose as the diaphragm for dialysis, a diaphragm for cells, etc. Among these, the diffusion dialysis using ion exchange membrane is economical separation technology with little energy expenditure which carries out separation recovery of these using the diffusion phenomenon of the acid by the concentration difference, or alkali. Therefore, applying this diffusion dialysis is increasing importance from viewpoints, such as effective use of environmental protection and a resource, in recent years as collection management technique of the waste acid which the discharge is increasing as industrial waste, or a spent caustic.

[0003] By the way, as for the ion exchange membrane used for diaphragms for dialysis, such as such a diffusion dialysis, excelling in a mechanical strength or chemical resistance is desirable, for this reason, porous membrane made of thermoplastics is used as a base material, and the film which filled up that opening section with ion exchange resin is used suitably. And ion exchange membrane which uses such porous membrane made of thermoplastics as a base material, For example, after it carries out impregnation of the monomer constituent which consists of the monomer which has a functional group suitable for installation of an ion exchange group, a cross linking agent, and a polymerization catalyst to this porous membrane made of thermoplastics and it carries out a polymerization to it, generally it is manufactured by the approach of introducing an ion exchange group, the method of carrying out impregnation of the solution made to dissolve ion exchange resin in a solvent to this porous membrane made of thermoplastics, and making a solvent remove, etc. (JP,6-329815,A, JP,1-22932,A, etc.).

[0004]

[Problem(s) to be Solved by the Invention] However, the ion exchange membrane obtained by the above approaches had the problem which cannot make water permeability unsatisfactorily small enough. That is, the above-mentioned ion exchange membrane was that with which the ion-exchange-resin solution or monomer constituent which carry out impregnation to the porous membrane made of thermoplastics cannot invade fully easily to the detailed section of the opening section of this base material, a volume change is also further produced since a solvent is removed after impregnation if it is in the approach of carrying out impregnation of the ion-exchange-resin solution, and ion exchange resin is hard to fill up into high density to the hole detailed section of this base material. Therefore, in such ion exchange membrane, the detailed hole where it does not fill up with the above-mentioned ion exchange resin densely remained a little, and, thereby, was not able to make membranous water permeability unsatisfactorily small enough like the above.

[0005] Then, when such ion exchange membrane was used as a diaphragm for dialysis, remarkable water penetrated the inside of the film toward the dilution room side during dialysis from the dialysis room side, the seepage flow of the acid which permeates a dialysis room from a raw material room side by this flow, or alkali was barred, and the problem to which the transmission rate of an acid or alkali falls had arisen. In the case of the diffusion dialysis to which osmosis of an acid or alkali is performed by only the diffusion phenomenon, especially lowering of this transmission rate was remarkable.

[0006] moreover, when a pressure differential arises between raw material room liquid and dialysis room liquid by fluctuation of the operating environment of the equipment under dialysis Transparency of the

water from the above-mentioned concentration room side to a dilution room side becomes strong further, or strong transparency of the water in a dilution room side to a concentration room side arises. In the case of the former The acid from the above-mentioned raw material room side to a dialysis room side and the transmission rate of alkali fall further. In the case of the latter The problem which accompanies to osmosis of this water and other impurity ion in a raw material room (it is polyvalent metal ion if it is recovery of the acid using anion exchange membrane and is recovery of the sodium hydroxide using a metal ion and cation exchange membrane) penetrates in a dialysis room was also produced.

[0007] As mentioned above, in the ion exchange membrane which uses sufficient thermoplastics nature porous membrane as a base material, and is excellent in a mechanical strength, water permeability was very small, and to develop the ion exchange membrane which can dialyze with the transmission rate of the acid which was excellent when it used as a diaphragm for diffusion dialyses, or alkali was desired.

[0008]

[Means for Solving the Problem] this invention person etc. has inquired wholeheartedly in view of the above-mentioned technical problem. Consequently, the product made of thermoplastics is used as a base material, and it succeeds in water permeability developing very small ion exchange membrane, and came to propose this invention.

[0009] That is, this invention is ion exchange membrane which uses porous membrane made of thermoplastics as a base material, and it is the ion exchange membrane with which it comes to fill up the opening section ion exchange resin, and thickness is 10–150 micrometers, and is characterized by the water permeability of the water in 25 degrees C being  $h/100$  or less kPa of  $5 \times 10^{-8} \text{ m}^3/$ .

[0010] Moreover, this invention also offers the diaphragm for diffusion dialyses which consists of the above-mentioned ion exchange membrane.

[0011] That is, the description of this invention is in ion exchange resin and the point of filling up with the so-called ion exchange resin of a hydrocarbon system especially, thoroughly substantially at the opening section by this free passage hole of the porous membrane made of thermoplastics. The water permeability of the ion exchange membrane of this invention can be set as the range of desired by the high hydrocarbon system ion exchange resin of the hydration force serving as ion exchange membrane of the gestalt distributed in the porous membrane made of thermoplastics in this way, raising the restoration nature of the ion exchange resin to this porous membrane made of thermoplastics, and adjusting ion exchange capacity and fixed ion concentration.

[0012] Here, thermoplastics is used without a limit of polyamide resin, such as fluorine system resin; nylon 6, such as vinyl chloride system resin; polytetrafluoroethylenes, such as a polyvinyl chloride, a vinyl chloride vinyl acetate copolymer, a vinyl chloride-vinylidene-chloride copolymer, and a vinyl chloride-olefine copolymer, poly trifluoro ethylene, polychlorotrifluoroethylene resin, Pori (tetrafluoroethylene-hexafluoropropylene), and Pori (tetrafluoroethylene-perfluoro-alkyl ether), and Nylon 66, etc. Since it has reached to an extreme to a mechanical strength, chemical stability, and chemical resistance, it is desirable especially to use polyolefin resin.

[0013] As polyolefin resin, the homopolymer or copolymers of an alpha olefin, such as ethylene, a propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 4-methyl-1-pentene, and a 5-methyl-1-heptene, are mentioned. Among these, in this invention, polyethylene and polypropylene are desirable and especially polyethylene is desirable. As for the weight average molecular weight of polyolefin resin, 10,000–500,000 are [ 10,000 or more ] suitably desirable.

[0014] Moreover, such porous membrane made of thermoplastics may have backing by the blanket-like object of the fiber made of polypropylene fiber \*\*\*\*\* thermoplastics further.

[0015] 0.05–5.0 micrometers, suitably, the average aperture of the hole of the above-mentioned porous membrane made of thermoplastics is 0.1–1.0 micrometers, and 40 – 90% of thing of voidage is more preferably desirable [ an aperture ] 30 to 95%. Since the transmission rate of an acid or alkali falls when an average aperture is 0.05 micrometers or less, and a mechanical strength becomes low when an average aperture is 5.0 micrometers or more, it is not desirable. Moreover, since the transmission rate of an acid or alkali falls when voidage is 30% or less, and a mechanical strength becomes low when voidage is 95% or more, it is not desirable.

[0016] Furthermore, the porous membrane made of thermoplastics has that desirable in which what has the thickness of 10–150 micrometers is desirable, and usually has the thickness of 20–120 micrometers more preferably from a viewpoint of giving a mechanical strength required as the viewpoint of raising a transmission rate and supporting lamella of an acid or alkali. That to which such porous membrane made of thermoplastics porosity-ized the film made of thermoplastics by the extending method etc. is used.

[0017] As for the ion exchange membrane of this invention, the opening section of the above-mentioned

porous membrane made of thermoplastics is filled up with ion exchange resin. Although it is not restricted especially if it is the functional group which can serve as negative or positive charge in a water solution as an ion exchange group of ion exchange resin, in the case of a cation-exchange radical, a sulfonic group, a carboxylic-acid radical, a phosphonic acid radical, etc. are mentioned, among these, specifically, especially a sulfonic group is desirable. Moreover, in the case of an anion-exchange radical, the 1-3rd class amino group, the 4th class ammonium, a pyridyl radical, an imidazole group, the 4th class pyridinium radical, etc. are mentioned, among these especially the 4th class pyridinium radical is desirable.

[0018] Although the ion exchange membrane of this invention is thin film which uses the porous membrane made of thermoplastics thin like the above as a base material, its water permeability is very small. That is, the water permeability in 25 degrees C is  $0.1-2 \times 10^{-8} \text{ m}^3/\text{h}/100 \text{ kPa}$  suitably  $h/100$  or less  $\text{kPa}$  of  $5 \times 10^{-8} \text{ m}^3/$ . Moreover, from the thickness of the above-mentioned base material, thickness has the thickness of 10-150 micrometers, and has the thickness of 20-120 micrometers preferably.

[0019] The ion exchange membrane of this invention can perform dialysis of an acid and alkali with the outstanding transmission rate, when this is used as the diaphragm for dialysis, especially a diaphragm for diffusion dialyses, since water permeability is very small in this way. In addition, it sets to this invention and the water permeability of ion exchange membrane is JIS. K It is measured using the pure-water water permeability testing device based on 3821.

[0020] That the water content in the inside of a 0.1 mol/L-sulfuric-acid water solution is 40 - 150% of value suitably 30 to 200% can make an acid and alkali penetrate with more sufficient transmission rate, and the ion exchange membrane of this invention has it. [ desirable ] The water content of such range is controllable by a class, ion exchange capacity, a degree of cross linking, etc. of the ion exchange group which the ion exchange resin which exists in the opening section of porous membrane has.

[0021] Furthermore, as for the ion exchange membrane of this invention, it is desirable that 0.2-5 or more mmol/g of ion exchange capacity is 0.5 - 3 mmol/g suitably.

[0022] the above -- although the ion exchange membrane of this invention in description may be manufactured by what kind of approach, generally it is manufactured by the following approaches. That is, after carrying out impregnation, carrying out reduced pressure deaeration of the monomer constituent which consists of the monomer, cross-linking monomer, and polymerization initiator which have the functional group or ion exchange group which can introduce an ion exchange group at the porous membrane made of thermoplastics, the polymerization of the monomer constituent is carried out and the approach of introducing a cation-exchange radical if needed is mentioned.

[0023] It is used in this manufacture approach, without limiting especially the hydrocarbon system monomer used in manufacture of conventionally well-known ion exchange resin as a monomer which has the monomer which has the functional group which can introduce an ion exchange group, or an ion exchange group. Specifically as a monomer which has the functional group which can introduce a cation-exchange radical, styrene, vinyltoluene, a vinyl xylene, alpha methyl styrene, vinyl naphthalene, and alpha-halogenation styrene are mentioned. Moreover, as a monomer which has a cation-exchange radical, phosphonic acid system monomers, such as carboxylic-acid system monomers, such as sulfonic-acid system monomers, such as alpha-halogenation vinyl sulfonic acid, a styrene sulfonic acid, and a vinyl sulfonic acid, a methacrylic acid, an acrylic acid, and a maleic anhydride, and a vinyl phosphoric acid, those salts, and ester are used.

[0024] As a monomer which, on the other hand, has the functional group which can introduce an anion-exchange radical, styrene, vinyltoluene, chloro methyl styrene, vinylpyridine, a vinyl imidazole, alpha methyl styrene, vinyl naphthalene, etc. are mentioned. Moreover, as a monomer which has an anion-exchange radical, nitrogen-containing heterocycle system monomers, such as amine system monomers, such as a vinylbenzyl trimethylamine and vinylbenzyl triethylamine, vinylpyridine, and a vinyl imidazole, those salts, and ester are used.

[0025] Moreover, especially as a cross-linking monomer, although not restricted, divinyl compounds, such as divinylbenzenes, a divinyl sulfone, a butadiene, a chloroprene, divinylbiphenyl, trivinylbenzene, divinyl naphthalene, a diaryl amine, and divinyl pyridines, are used, for example.

[0026] In this invention, these monomers, other monomers which can be copolymerized, and plasticizers other than the monomer which has the monomer which has the functional group which can introduce the above-mentioned ion exchange group, or an ion exchange group, or a cross-linking monomer may be added if needed. As other monomers carried out like this, styrene, acrylonitrile, methyl styrene, an acrolein, a methyl vinyl ketone, a vinyl biphenyl, etc. are used, for example. Moreover, as plasticizers, dibutyl phthalate, dioctyl phthalate, dimethyl isophthalate, a dibutyl horse mackerel peat, triethyl SHITORETO, acetyl tributyl citrate, dibutyl sebacate, etc. are used.

[0027] Next, as a polymerization initiator in this invention, a well-known thing is conventionally used especially without a limit. As an example of such a polymerization initiator, organic peroxide, such as octanoyl peroxide, lauroyl peroxide, t-butylperoxy-2-ethylhexanoate, benzoyl peroxide, t-buthylperoxy isobuthylate, t-butyl peroxy laurate, t-hexyl peroxy benzoate, and G t-butyl peroxide, is used.

[0028] In this invention, the blending ratio of each component which constitutes a monomer constituent. In order to attain the object of this invention, generally As opposed to the monomer 100 weight section which has the monomer which has the functional group which can introduce an ion exchange group, or an ion exchange group It is suitable to carry out the 0-50 weight section activity of the cross-linking monomer to the above-mentioned monomer, when adding the 0 - 100 weight section and plasticizers for 1 - 40 weight section, and these monomers and other monomers which can be copolymerized suitably, 0.1 - 50 weight section and. Moreover, a polymerization initiator has and carries out monomer 100 weight \*\*\*\* of the monomer or ion exchange group which has the functional group which can introduce an ion exchange group, and it is desirable 0.1 - 20 weight section and to carry out 0.5-10 weight section combination suitably.

[0029] the approach that the restoration approach of the above-mentioned monomer constituent to the porous membrane made of thermoplastics which is a base material can be densely filled up with a monomer constituent to the detailed section of the hole of this porous membrane -- if it can kick, it will not become. It is suitable to adopt the approach of carrying out impregnation, carrying out reduced pressure deaeration of the above-mentioned monomer constituent at the porous membrane made of thermoplastics. Thus, if impregnation is deaerated and carried out under reduced pressure, it will become possible for you to make it filled up with a monomer constituent without a clearance to the detailed section of the opening section. And the ion exchange membrane which carried out the polymerization of the monomer constituent turns into film of description with very small water permeability which said invention in this application specifies after this impregnation.

[0030] Here, impregnation processing while [ above-mentioned ] carrying out reduced pressure deaeration is contacted under the reduced pressure to the porous membrane made of thermoplastics of a monomer constituent, and, specifically, is performed by returning a pressure to atmospheric pressure. For example, the porous membrane made of thermoplastics is immersed in the method of making monomer mixture introduced and immersed in a container, after putting the porous membrane made of thermoplastics into a container and changing into a reduced pressure condition with a vacuum pump until it returns to atmospheric pressure, or the monomer mixture put into the container, and after carrying out reduced pressure deaeration of the gas in a hole with a vacuum pump, the approach of returning to atmospheric pressure etc. is mentioned. Whenever [ reduced pressure / when decompressing ] has a desirable pressure until a monomer boils under 7kPa - working temperature, and it is desirable to adopt from the range of 2kPa-0.1kPa especially. What is necessary is for the temperature at the time of impregnation to have common 20 degrees C or less, and just to usually adopt impregnation time amount suitably in the range for 5 - 60 minutes.

[0031] In order to carry out an after polymerization, the approach of inserting into films, such as polyester, generally and carrying out temperature up from ordinary temperature under application of pressure with which the porous membrane made of thermoplastics was made to fill up as the monomer constituent was described above is desirable. What is necessary is for such polymerization conditions not to be influenced by the presentation of the class of polymerization initiator which involves, and a monomer constituent etc., not to limit them especially, and just to choose them suitably.

[0032] If needed, if the filmy material which a polymerization is carried out as mentioned above and obtained is well-known cation exchange membrane about this and they are processing of sulfonation, the Krol sulfonation, phosphonium-izing, hydrolysis, etc., and anion exchange membrane, it can introduce a desired ion exchange group by processing of amination, alkylation, etc., and can use it as ion exchange membrane.

[0033]

[Effect of the Invention] The ion exchange membrane of this invention has very small water permeability, although thickness is the thin film which is 10-150 micrometers, since it fills up with the ion exchange resin which was excellent in a mechanical strength or chemical resistance, and constructed the bridge over the opening section of the porous membrane made of thermoplastics without the clearance to the detailed section. Therefore, when it uses as diaphragms for dialysis, such as electrodialysis and a diffusion dialysis, especially a diaphragm for diffusion dialyses, an acid and alkali can be made to be able to penetrate with the outstanding transmission rate, and efficient dialysis can be performed. Moreover, since it fills up with ion exchange resin densely to the opening section detailed section of the porous membrane made of

thermoplastics in this way, the transparency of other impurity ion which leads hardly produce the opening which remains inside, but an acid and alkali can be made to penetrate by good permselectivity.

[0034] Furthermore, it is prevented that a big change does not arise in the membranous amount of water penetration, but the further lowering of the transmission rate of the above-mentioned acid or alkali and the transparency to the dialysis room of other impurity ion become strong by fluctuation of the operating environment under dialysis even when a pressure differential arises between raw material room liquid and dialysis room liquid.

[0035] therefore, \*\* — the ion exchange membrane of this invention which has description [ like ] can be suitably used as the above-mentioned diaphragm for diffusion dialyses. In that case, as an acid dialyzed using anion exchange membrane, a sulfuric acid, a hydrochloric acid, a nitric acid, \*\* fluoric acid, a phosphoric acid, etc. are mentioned, and a sodium hydroxide, a potassium hydroxide, etc. are mentioned as alkali dialyzed using another side and cation exchange membrane. Especially applying is desirable, in case the industrial effluent which such acids and alkali contain is made into a processed liquid and an acid and alkali are collected from these. Moreover, the ion exchange membrane of this invention can be used good in the activity field of the ion exchange membrane which makes the ion in water solutions, such as film separators, such as a diaphragm for dialysis of others, such as electrodialysis, and a redox flow cell, and for ion sensors, penetrate using description with small water permeability.

[0036]

[Example] Although an example is hereafter given in order to explain this invention to a detail further, this invention is not limited to these examples.

[0037] In addition, the measuring method of the ion exchange capacity used for the characterization of ion exchange membrane in the example and the example of a comparison, water content, water permeability, and a matter transmission rate is explained below.

[0038] 1) Ion exchange capacity and water content ion exchange membrane are immersed in 1 mol/L-HCl for 10 hours or more.

[0039] Then, the hydrogen ion mold was made to permute by the sodium ion mold by 1 mol/L-NaCl in the case of cation exchange membrane, and the quantum of the hydrogen ion which separated was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol). On the other hand, the chloride-ion mold was made to permute by the nitrate ion mold by 1 mol/L-NaNO<sub>3</sub> in the case of anion exchange membrane, and the quantum of the chloride ion which separated was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol).

[0040] Next, after being immersed in 1 mol/L-HCl for 4 hours or more and fully rinsing the same ion exchange membrane with ion exchange water, surface moisture was wiped off for the film with ejection tissue paper etc., and the weight at the time of humidity (Wg) was measured. Next, the film was put into the reduced-pressure-drying machine, and it was made to dry at 60 degrees C for 5 hours. The weight at the time of ejection desiccation (Dg) was measured for the film.

[0041] Ion exchange capacity and water content were computed by the degree type.

[0042] Ion exchange capacity =  $A \times 1000 / W$  [mmol/g-desiccation film]

Water content =  $100 \times (W - D) / D$  [%]

2) Water permeability JIS K The pure-water water permeability testing device based on 3821 was used. In 25 degrees C, the pure-water water permeability testing device was equipped with the ion exchange membrane used for measurement by the moisture state. Water permeability was searched for by the degree type.

[0043]  $C = Q_{25} / PC$ : Permeable [m<sup>3</sup>/h/100kPa]

The transparency flow rate of the water in Q<sub>25</sub>: 25 degree C [m<sup>3</sup>/h]

P: Average film differential pressure [kPa]

3) In the transmission rate anion exchange membrane of an acid and alkali, the liquid which contains 25-degree C one mol / L-sulfuric acid, and 0.5 mol/L-magnesium sulfate in one room (undiluted solution room) was put in using the two-room cel made of acrylic resin divided by anion exchange membrane, and 25-degree C ion exchange water was put into one more room (dialysing fluid room). Both \*\* were stirred by the stirring child, the liquid of a dialysing fluid room was sampled after fixed time amount, the amount of transparency of a sulfuric acid was measured with potentiometric titration, and the amount of transparency of magnesium sulfate was measured with the atomic absorption spectro-photometer, respectively.

[0044] Moreover, in cation exchange membrane, in the above-mentioned approach, the liquid containing a 1 mol/L-sulfuric acid and 0.5 mol/L-magnesium sulfate was replaced with the liquid containing a 3 mol/L-sodium hydroxide and a 0.5 mol/L-aluminum hydroxide, same actuation was performed, and the amount of transparency of a sodium hydroxide and an aluminum hydroxide was measured. It asked for the

transmission rate of each matter by degree type.

[0045]  $U=A/(T-S \text{ and } **C)$

U: The transmission rate of an acid or alkali [mol/Hr-m<sup>2</sup>- (mol/L)]

A: An acid or the amount of transparency of alkali [mol]

T: Mixing time [Hr]

S: Effective film surface product [m<sup>2</sup>]

\*\*C: The acid of both \*\* before and behind stirring, or the logarithmic-mean concentration difference of alkali [mol/L]

According to the presentation table having shown in one to example 5 table 1, various monomers etc. were mixed and the monomer constituent was obtained. 400g of obtained monomer constituents was put into 500ml glassware, and the porous membrane made from polyethylene of weight average molecular weight 100,000 (A, B, C, D, every 20cmx 20cm) and the porous membrane made from polypropylene of weight average molecular weight 150,000 (E, 20cmx20cm) were immersed.

[0046] Next, glassware was made reduced pressure for 10 minutes to the pressure of 0.7kPa(s) with the vacuum pump, after carrying out reduced pressure deaeration, it returned to ordinary pressure and the hole of porous membrane was filled up with the monomer constituent. Then, after covering the both sides of porous membrane, having used ejection and 100-micrometer polyester film as exfoliation material for porous membrane out of the monomer constituent, the heating polymerization was carried out at 80 degrees C under the nitrogen application of pressure of 0.4MPa for 8 hours.

[0047] The obtained filmy material was immersed at 30 degrees C into the mixture of 1:4 of a methyl iodide and a methanol for 24 hours, and pyridinium mold anion exchange membrane was obtained.

[0048] The thickness of such pyridinium mold anion exchange membrane, ion exchange capacity, water content, water permeability, and a matter transmission rate were measured. These results were shown in a table 2.

[0049] Except having not performed reduced pressure deaeration actuation in example of comparison 1 example 1, the same actuation as an example 1 was performed and pyridinium mold anion exchange membrane was obtained.

[0050] The thickness of this pyridinium mold anion exchange membrane, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were measured. This result was shown in a table 2.

[0051] Thickness, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were similarly measured using the anion exchange membrane (commercial item A; Tokuyama make) marketed example of comparison 2. The result was shown in a table 2.

[0052] Example of comparison 3 polyethylene porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyethylene porous membrane was dried at ejection and 50 degrees C out of liquid. After repeating this actuation 5 times, reduced pressure drying was carried out at 80 degrees C for 2 hours, and the filmy material was obtained.

[0053] Methyl alcohol washed, after being immersed in the chloromethyl methyl ether which added 2% of the weight of anhydrous salt-ized tin and making the obtained filmy material react at 35 degrees C for 4 hours.

[0054] Next, the filmy material which chloromethylated was made to react to the mixed solution of 20:30:50 of a trimethylamine, an acetone, and ion exchange water at 30 degrees C 30% for 24 hours, and the anion exchange membrane which has a quaternary ammonium base as an ion exchange group was obtained.

[0055] The thickness of this anion exchange membrane, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were measured. The result was shown in a table 2.

[0056] According to the presentation table having shown in six to example 10 table 1, the same impregnation as examples 1-5 and polymerization actuation were performed, the obtained filmy material was immersed for 45 minutes at 40 degrees C into the mixture of 1:1 of 98% concentrated sulfuric acid and the chlorosulfonic acid of 90% or more of purity, and sulfonic acid type cation exchange membrane was obtained.

[0057] The thickness of such sulfonic acid type cation exchange membrane, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were measured. These results were shown in a table 3.

[0058] Except having not performed reduced pressure deaeration actuation in example of comparison 4 example 6, the same actuation as an example 6 was performed and sulfonic acid type cation exchange membrane was obtained.

[0059] The thickness of this sulfonic acid type cation exchange membrane, ion exchange capacity, water

content, water permeability, and a NaOH transmission rate were measured. The result was shown in a table 3.

[0060] Thickness, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were similarly measured using the cation exchange membrane (commercial item B; Tokuyama make) marketed example of comparison 5. The result was shown in a table 3.

[0061] Example of comparison 6 polyethylene porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyethylene porous membrane was dried at ejection and 50 degrees C out of liquid. After repeating this actuation 5 times, reduced pressure drying was carried out at 80 degrees C for 2 hours, and the filmy material was obtained.

[0062] The obtained filmy material was immersed for 60 minutes at 40 degrees C into 98% concentrated sulfuric acid, and sulfonic acid type cation exchange membrane was obtained. The thickness of this sulfonic acid type cation exchange membrane, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were measured. These results were shown in a table 3.

[0063]

[A table 1]

表1

| 実施例No. | 多孔質膜 <sup>1)</sup> | 組成(重量比)          |                    |                   |                    |                  |
|--------|--------------------|------------------|--------------------|-------------------|--------------------|------------------|
|        |                    | St <sup>2)</sup> | 4-VP <sup>3)</sup> | DVB <sup>4)</sup> | ATBC <sup>5)</sup> | PO <sup>6)</sup> |
| 1      | A                  |                  | 80                 | 7                 | 5                  | 5                |
| 2      | B                  |                  | 80                 | 7                 | 5                  | 5                |
| 3      | C                  |                  | 80                 | 7                 | 5                  | 5                |
| 4      | D                  |                  | 80                 | 7                 | 5                  | 5                |
| 5      | E                  |                  | 80                 | 7                 | 5                  | 5                |
| 6      | A                  | 80               |                    | 7                 | 10                 | 5                |
| 7      | B                  | 80               |                    | 7                 | 10                 | 5                |
| 8      | C                  | 80               |                    | 7                 | 10                 | 5                |
| 9      | D                  | 80               |                    | 7                 | 10                 | 5                |
| 10     | E                  | 80               |                    | 7                 | 10                 | 5                |

1) 多孔質膜

A: ポリエチレン製、膜厚25  $\mu\text{m}$ 、空隙率45%、平均孔径0.5  $\mu\text{m}$

B: ポリエチレン製、膜厚50  $\mu\text{m}$ 、空隙率60%、平均孔径0.5  $\mu\text{m}$

C: ポリエチレン製、膜厚70  $\mu\text{m}$ 、空隙率80%、平均孔径0.5  $\mu\text{m}$

D: ポリエチレン製、膜厚100  $\mu\text{m}$ 、空隙率80%、平均孔径0.5  $\mu\text{m}$

E: ポリプロピレン製、膜厚50  $\mu\text{m}$ 、空隙率70%、平均孔径0.2  $\mu\text{m}$

2) スチレン

3) 4-ビニルピリジン

4) ジビニルベンゼン

5) アセチルクエン酸トリブチル

6) t-ブチルパーオキシエチルヘキサノエート

[0064]

[A table 2]

表2

| 実施例No. | 膜厚  | イオン交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度                                   |                           |
|--------|-----|---------|-----|----------------------|--|---------------------------|
|        |     |         |     |                      | H <sub>2</sub> SO <sub>4</sub><br>透過速度 | MgSO <sub>4</sub><br>透過速度 |
| 1      | 32  | 2.6     | 68  | 1.2                  | 26                                     | 0.091                     |
| 2      | 63  | 2.7     | 70  | 0.9                  | 22                                     | 0.083                     |
| 3      | 87  | 3.1     | 72  | 0.6                  | 18                                     | 0.076                     |
| 4      | 115 | 3.2     | 80  | 0.6                  | 15                                     | 0.066                     |
| 5      | 58  | 2.5     | 68  | 0.8                  | 20                                     | 0.078                     |
| 比較例1   | 30  | 1.6     | 55  | 29.2                 | 12                                     | 1.035                     |
| 比較例2   | 150 | 3.5     | 80  | 7.0                  | 6                                      | 0.101                     |
| 比較例3   | 29  | 0.2     | 30  | 82.4                 | 9                                      | 2.024                     |

膜厚[ $\mu\text{m}$ ]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

H<sub>2</sub>SO<sub>4</sub>透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]

MgSO<sub>4</sub>透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]

透水性[ $\text{m}^3/\text{Hr}/100\text{kPa}$ ]

選択透過性[ - ]

[0065]

[A table 3]



表3

| 実施例No. | 膜厚  | イオン<br>交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度         |                             |
|--------|-----|-------------|-----|----------------------|--------------|-----------------------------|
|        |     |             |     |                      | NaOH<br>透過速度 | Al(OH) <sub>3</sub><br>透過速度 |
| 6      | 35  | 2.7         | 59  | 1.3                  | 5.2          | 0.072                       |
| 7      | 62  | 2.6         | 58  | 0.8                  | 4.6          | 0.061                       |
| 8      | 88  | 3.0         | 69  | 0.6                  | 4.2          | 0.049                       |
| 9      | 114 | 3.1         | 72  | 0.4                  | 3.8          | 0.033                       |
| 10     | 59  | 2.6         | 62  | 0.8                  | 4.7          | 0.055                       |
| 比較例4   | 31  | 2.1         | 60  | 50.7                 | 3.3          | 0.986                       |
| 比較例5   | 180 | 2.5         | 51  | 8.8                  | 1.2          | 0.572                       |
| 比較例6   | 31  | 0.2         | 32  | 70.4                 | 3            | 0.802                       |

膜厚[ $\mu\text{m}$ ]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

NaOH透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]Al(OH)<sub>3</sub>透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]透水性[ $\text{m}^3/\text{Hr}/100\text{kPa}$ ]

選択透過性[-]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the ion exchange membrane used for the diaphragm for dialysis, the diaphragm for cells, a sensor, etc., especially the ion exchange membrane suitably used as a diaphragm for diffusion dialyses.

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**PRIOR ART**

[Description of the Prior Art] Ion exchange membrane is used general-purpose as the diaphragm for dialysis, a diaphragm for cells, etc. Among these, the diffusion dialysis using ion exchange membrane is economical separation technology with little energy expenditure which carries out separation recovery of these using the diffusion phenomenon of the acid by the concentration difference, or alkali. Therefore, applying this diffusion dialysis is increasing importance from viewpoints, such as effective use of environmental protection and a resource, in recent years as collection management technique of the waste acid which the discharge is increasing as industrial waste, or a spent caustic.

[0003] By the way, as for the ion exchange membrane used for diaphragms for dialysis, such as such a diffusion dialysis, excelling in a mechanical strength or chemical resistance is desirable, for this reason, porous membrane made of thermoplastics is used as a base material, and the film which filled up that opening section with ion exchange resin is used suitably. And ion exchange membrane which uses such porous membrane made of thermoplastics as a base material, For example, after it carries out impregnation of the monomer constituent which consists of the monomer which has a functional group suitable for installation of an ion exchange group, a cross linking agent, and a polymerization catalyst to this porous membrane made of thermoplastics and it carries out a polymerization to it, generally it is manufactured by the approach of introducing an ion exchange group, the method of carrying out impregnation of the solution made to dissolve ion exchange resin in a solvent to this porous membrane made of thermoplastics, and making a solvent remove, etc. (JP,6-329815,A, JP,1-22932,A, etc.).

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## EFFECT OF THE INVENTION

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[Effect of the Invention] The ion exchange membrane of this invention has very small water permeability, although thickness is the thin film which is 10-150 micrometers, since it fills up with the ion exchange resin which was excellent in a mechanical strength or chemical resistance, and constructed the bridge over the opening section of the porous membrane made of thermoplastics without the clearance to the detailed section. Therefore, when it uses as diaphragms for dialysis, such as electrodialysis and a diffusion dialysis, especially a diaphragm for diffusion dialyses, an acid and alkali can be made to be able to penetrate with the outstanding transmission rate, and efficient dialysis can be performed. Moreover, since it fills up with ion exchange resin densely to the opening section detailed section of the porous membrane made of thermoplastics in this way, the transparency of other impurity ion which leads can hardly produce the opening which remains inside, but an acid and alkali can be made to penetrate by good permselectivity. [0034] Furthermore, it is prevented that a big change does not arise in the membranous amount of water penetration, but the further lowering of the transmission rate of the above-mentioned acid or alkali and the transparency to the dialysis room of other impurity ion become strong by fluctuation of the operating environment under dialysis even when a pressure differential arises between raw material room liquid and dialysis room liquid.

[0035] therefore, \*\* -- the ion exchange membrane of this invention which has description [ like ] can be suitably used as the above-mentioned diaphragm for diffusion dialyses. In that case, as an acid dialyzed using anion exchange membrane, a sulfuric acid, a hydrochloric acid, a nitric acid, \*\* fluoric acid, a phosphoric acid, etc. are mentioned, and a sodium hydroxide, a potassium hydroxide, etc. are mentioned as alkali dialyzed using another side and cation exchange membrane. Especially applying is desirable, in case the industrial effluent which such acids and alkali contain is made into a processed liquid and an acid and alkali are collected from these. Moreover, the ion exchange membrane of this invention can be used good in the activity field of the ion exchange membrane which makes the ion in water solutions, such as film separators, such as a diaphragm for dialysis of others, such as electrodialysis, and a redox flow cell, and for ion sensors, penetrate using description with small water permeability.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, the ion exchange membrane obtained by the above approaches had the problem which cannot make water permeability unsatisfactorily small enough. That is, the above-mentioned ion exchange membrane was that with which the ion-exchange-resin solution or monomer constituent which carry out impregnation to the porous membrane made of thermoplastics cannot invade fully easily to the detailed section of the opening section of this base material, a volume change is also further produced since a solvent is removed after impregnation if it is in the approach of carrying out impregnation of the ion-exchange-resin solution, and ion exchange resin is hard to fill up into high density to the hole detailed section of this base material. Therefore, in such ion exchange membrane, the detailed hole where it does not fill up with the above-mentioned ion exchange resin densely remained a little, and, thereby, was not able to make membranous water permeability unsatisfactorily small enough like the above.

[0005] Then, when such ion exchange membrane was used as a diaphragm for dialysis, remarkable water penetrated the inside of the film toward the dilution room side during dialysis from the dialysis room side, the seepage flow of the acid which permeates a dialysis room from a raw material room side by this flow, or alkali was barred, and the problem to which the transmission rate of an acid or alkali falls had arisen. In the case of the diffusion dialysis to which osmosis of an acid or alkali is performed by only the diffusion phenomenon, especially lowering of this transmission rate was remarkable.

[0006] moreover, when a pressure differential arises between raw material room liquid and dialysis room liquid by fluctuation of the operating environment of the equipment under dialysis Transparency of the water from the above-mentioned concentration room side to a dilution room side becomes strong further, or strong transparency of the water from a dilution room side to a concentration room side arises. In the case of the former The acid from the above-mentioned raw material room side to a dialysis room side and the transmission rate of alkali fall further. In the case of the latter The problem which accompanies to osmosis of this water and other impurity ion in a raw material room (it is polyvalent metal ion if it is recovery of the acid using anion exchange membrane and is recovery of the sodium hydroxide using a metal ion and cation exchange membrane) penetrates in a dialysis room was also produced.

[0007] As mentioned above, in the ion exchange membrane which uses sufficient thermoplastics nature porous membrane as a base material, and is excellent in a mechanical strength, water permeability was very small, and to develop the ion exchange membrane which can dialyze with the transmission rate of the acid which was excellent when it used as a diaphragm for diffusion dialyses, or alkali was desired.

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MEANS

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[Means for Solving the Problem] this invention person etc. has inquired wholeheartedly in view of the above-mentioned technical problem. Consequently, the product made of thermoplastics is used as a base material, and it succeeds in water permeability developing very small ion exchange membrane, and came to propose this invention.

[0009] That is, this invention is ion exchange membrane which uses porous membrane made of thermoplastics as a base material, and it is the ion exchange membrane with which it comes to fill up the opening section ion exchange resin, and thickness is 10-150 micrometers, and is characterized by the water permeability of the water in 25 degrees C being  $h/100$  or less kPa of  $5 \times 10^{-8} m^3$ .

[0010] Moreover, this invention also offers the diaphragm for diffusion dialyses which consists of the above-mentioned ion exchange membrane.

[0011] That is, the description of this invention is in ion exchange resin and the point of filling up with the so-called ion exchange resin of a hydrocarbon system especially, thoroughly substantially at the opening section by this free passage hole of the porous membrane made of thermoplastics. The water permeability of the ion exchange membrane of this invention can be set as the range of desired by the high hydrocarbon system ion exchange resin of the hydration force serving as ion exchange membrane of the gestalt distributed in the porous membrane made of thermoplastics in this way, raising the restoration nature of the ion exchange resin to this porous membrane made of thermoplastics, and adjusting ion exchange capacity and fixed ion concentration.

[0012] Here, thermoplastics is used without a limit of polyamide resin, such as fluorine system resin; nylon 6, such as vinyl chloride system resin; polytetrafluoroethylenes, such as a polyvinyl chloride, a vinyl chloride vinyl acetate copolymer, a vinyl chloride-vinylidene-chloride copolymer, and a vinyl chloride-olefine copolymer, poly trifluoro ethylene, polychlorotrifluoroethylene resin, Pori (tetrafluoroethylene-hexafluoropropylene), and Pori (tetrafluoroethylene-perfluoro-alkyl ether), and Nylon 66, etc. Since it has reached to an extreme to a mechanical strength, chemical stability, and chemical resistance, it is desirable especially to use polyolefin resin.

[0013] As polyolefin resin, the homopolymer or copolymers of an alpha olefin, such as ethylene, a propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 4-methyl-1-pentene, and a 5-methyl-1-heptene, are mentioned. Among these, in this invention, polyethylene and polypropylene are desirable and especially polyethylene is desirable. As for the weight average molecular weight of polyolefin resin, 10,000-500,000 are [ 10,000 or more ] suitably desirable.

[0014] Moreover, such porous membrane made of thermoplastics may have backing by the blanket-like object of the fiber made of polypropylene fiber \*\*\*\*\* thermoplastics further.

[0015] 0.05-5.0 micrometers, suitably, the average aperture of the hole of the above-mentioned porous membrane made of thermoplastics is 0.1-1.0 micrometers, and 40 - 90% of thing of voidage is more preferably desirable [ an aperture ] 30 to 95%. Since the transmission rate of an acid or alkali falls when an average aperture is 0.05 micrometers or less, and a mechanical strength becomes low when an average aperture is 5.0 micrometers or more, it is not desirable. Moreover, since the transmission rate of an acid or alkali falls when voidage is 30% or less, and a mechanical strength becomes low when voidage is 95% or more, it is not desirable.

[0016] Furthermore, the porous membrane made of thermoplastics has that desirable in which what has the thickness of 10-150 micrometers is desirable, and usually has the thickness of 20-120 micrometers more preferably from a viewpoint of giving a mechanical strength required as the viewpoint of raising a transmission rate and supporting lamella of an acid or alkali. That to which such porous membrane made of thermoplastics porosity-ized the film made of thermoplastics by the extending method etc. is used.

[0017] As for the ion exchange membrane of this invention, the opening section of the above-mentioned porous membrane made of thermoplastics is filled up with ion exchange resin. Although it is not restricted especially if it is the functional group which can serve as negative or positive charge in a water solution as an ion exchange group of ion exchange resin, in the case of a cation-exchange radical, a sulfonic group, a carboxylic-acid radical, a phosphonic acid radical, etc. are mentioned, among these, specifically, especially a sulfonic group is desirable. Moreover, in the case of an anion-exchange radical, the 1-3rd class amino group, the 4th class ammonium, a pyridyl radical, an imidazole group, the 4th class pyridinium radical, etc. are mentioned, among these especially the 4th class pyridinium radical is desirable.

[0018] Although the ion exchange membrane of this invention is thin film which uses the porous membrane made of thermoplastics thin like the above as a base material, its water permeability is very small. That is, the water permeability in 25 degrees C is  $0.1-2 \times 10^{-8} \text{ m}^3/\text{h}/100\text{kPa}$  suitably  $h/100$  or less  $\text{kPa}$  of  $5 \times 10^{-8} \text{ m}^3/$ . Moreover, from the thickness of the above-mentioned base material, thickness has the thickness of 10-150 micrometers, and has the thickness of 20-120 micrometers preferably.

[0019] The ion exchange membrane of this invention can perform dialysis of an acid and alkali with the outstanding transmission rate, when this is used as the diaphragm for dialysis, especially a diaphragm for diffusion dialyses, since water permeability is very small in this way. In addition, it sets to this invention and the water permeability of ion exchange membrane is JIS. K It is measured using the pure-water water permeability testing device based on 3821.

[0020] That the water content in the inside of a 0.1 mol/L-sulfuric-acid water solution is 40 - 150% of value suitably 30 to 200% can make an acid and alkali penetrate with more sufficient transmission rate, and the ion exchange membrane of this invention has it. [ desirable ] The water content of such range is controllable by a class, ion exchange capacity, a degree of cross linking, etc. of the ion exchange group which the ion exchange resin which exists in the opening section of porous membrane has.

[0021] Furthermore, as for the ion exchange membrane of this invention, it is desirable that 0.2-5 or more mmol/g of ion exchange capacity is 0.5 - 3 mmol/g suitably.

[0022] the above — although the ion exchange membrane of this invention in description may be manufactured by what kind of approach, generally it is manufactured by the following approaches. That is, after carrying out impregnation, carrying out reduced pressure deaeration of the monomer constituent which consists of the monomer, cross-linking monomer, and polymerization initiator which have the functional group or ion exchange group which can introduce an ion exchange group at the porous membrane made of thermoplastics, the polymerization of the monomer constituent is carried out and the approach of introducing a cation-exchange radical if needed is mentioned.

[0023] It is used in this manufacture approach, without limiting especially the hydrocarbon system monomer used in manufacture of conventionally well-known ion exchange resin as a monomer which has the monomer which has the functional group which can introduce an ion exchange group, or an ion exchange group. Specifically as a monomer which has the functional group which can introduce a cation-exchange radical, styrene, vinyltoluene, a vinyl xylene, alpha methyl styrene, vinyl naphthalene, and alpha-halogenation styrene are mentioned. Moreover, as a monomer which has a cation-exchange radical, phosphonic acid system monomers, such as carboxylic-acid system monomers, such as sulfonic-acid system monomers, such as alpha-halogenation vinyl sulfonic acid, a styrene sulfonic acid, and a vinyl sulfonic acid, a methacrylic acid, an acrylic acid, and a maleic anhydride, and a vinyl phosphoric acid, those salts, and ester are used.

[0024] As a monomer which, on the other hand, has the functional group which can introduce an anion-exchange radical, styrene, vinyltoluene, chloro methyl styrene, vinylpyridine, a vinyl imidazole, alpha methyl styrene, vinyl naphthalene, etc. are mentioned. Moreover, as a monomer which has an anion-exchange radical, nitrogen-containing heterocycle system monomers, such as amine system monomers, such as a vinylbenzyl trimethylamine and vinylbenzyl triethylamine, vinylpyridine, and a vinyl imidazole, those salts, and ester are used.

[0025] Moreover, especially as a cross-linking monomer, although not restricted, divinyl compounds, such as divinylbenzenes, a divinyl sulfone, a butadiene, a chloroprene, divinylbiphenyl, trivinylbenzene, divinyl naphthalene, a diaryl amine, and divinyl pyridines, are used, for example.

[0026] In this invention, these monomers, other monomers which can be copolymerized, and plasticizers other than the monomer which has the monomer which has the functional group which can introduce the above-mentioned ion exchange group, or an ion exchange group, or a cross-linking monomer may be added if needed. As other monomers carried out like this, styrene, acrylonitrile, methyl styrene, an acrolein, a methyl vinyl ketone, a vinyl biphenyl, etc. are used, for example. Moreover, as plasticizers, dibutyl phthalate, dioctyl phthalate, dimethyl isophthalate, a dibutyl horse mackerel peat, triethyl SHITORETO, acetyl tributyl

citrate, dibutyl sebacate, etc. are used.

[0027] Next, as a polymerization initiator in this invention, a well-known thing is conventionally used especially without a limit. As an example of such a polymerization initiator, organic peroxide, such as octanoyl peroxide, lauroyl peroxide, t-butylperoxy-2-ethylhexanoate, benzoyl peroxide, t-butylperoxy isobutylate, t-butyl peroxy laurate, t-hexyl peroxy benzoate, and G t-butyl peroxide, is used.

[0028] In this invention, the blending ratio of each component which constitutes a monomer constituent. In order to attain the object of this invention, generally as opposed to the monomer 100 weight section which has the monomer which has the functional group which can introduce an ion exchange group, or an ion exchange group. It is suitable to carry out the 0-50 weight section activity of the cross-linking monomer to the above-mentioned monomer, when adding the 0 - 100 weight section and plasticizers for 1 - 40 weight section, and these monomers and other monomers which can be copolymerized suitably, 0.1 - 50 weight section and. Moreover, a polymerization initiator has and carries out monomer 100 weight \*\*\*\* of the monomer or ion exchange group which has the functional group which can introduce an ion exchange group, and it is desirable 0.1 - 20 weight section and to carry out 0.5-10 weight section combination suitably.

[0029] the approach that the restoration approach of the above-mentioned monomer constituent to the porous membrane made of thermoplastics which is a base material can be densely filled up with a monomer constituent to the detailed section of the hole of this porous membrane — if it can kick, it will not become. It is suitable to adopt the approach of carrying out impregnation, carrying out reduced pressure deaeration of the above-mentioned monomer constituent at the porous membrane made of thermoplastics. Thus, if impregnation is deaerated and carried out under reduced pressure, it will become possible for you to make it filled up with a monomer constituent without a clearance to the detailed section of the opening section. And the ion exchange membrane which carried out the polymerization of the monomer constituent turns into film of description with very small water permeability which said invention in this application specifies after this impregnation.

[0030] Here, impregnation processing while [ above-mentioned ] carrying out reduced pressure deaeration is contacted under the reduced pressure to the porous membrane made of thermoplastics of a monomer constituent, and, specifically, is performed by returning a pressure to atmospheric pressure. For example, the porous membrane made of thermoplastics is immersed in the method of making monomer mixture introduced and immersed in a container, after putting the porous membrane made of thermoplastics into a container and changing into a reduced pressure condition with a vacuum pump until it returns to atmospheric pressure, or the monomer mixture put into the container, and after carrying out reduced pressure deaeration of the gas in a hole with a vacuum pump, the approach of returning to atmospheric pressure etc. is mentioned. Whenever [ reduced pressure / when decompressing ] has a desirable pressure until a monomer boils under 7kPa - working temperature, and it is desirable to adopt from the range of 2kPa-0.1kPa especially. What is necessary is for the temperature at the time of impregnation to have common 20 degrees C or less, and just to usually adopt impregnation time amount suitably in the range for 5 - 60 minutes.

[0031] In order to carry out an after polymerization, the approach of inserting into films, such as polyester, generally and carrying out temperature up from ordinary temperature under application of pressure with which the porous membrane made of thermoplastics was made to fill up as the monomer constituent was described above is desirable. What is necessary is for such polymerization conditions not to be influenced, by the presentation of the class of polymerization initiator which involves, and a monomer constituent etc., not to limit them especially, and just to choose them suitably.

[0032] If needed, if the filmy material which a polymerization is carried out as mentioned above and obtained is well-known cation exchange membrane about this and they are processing of sulfonation, the Krol sulfonation, phosphonium-izing, hydrolysis, etc., and anion exchange membrane, it can introduce a desired ion exchange group by processing of amination, alkylation, etc., and can use it as ion exchange membrane.

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## EXAMPLE

[Example] Although an example is hereafter given in order to explain this invention to a detail further, this invention is not limited to these examples.

[0037] In addition, the measuring method of the ion exchange capacity used for the characterization of ion exchange membrane in the example and the example of a comparison, water content, water permeability, and a matter transmission rate is explained below.

[0038] 1) Ion exchange capacity and water content ion exchange membrane are immersed in 1 mol/L-HCl for 10 hours or more.

[0039] Then, the hydrogen ion mold was made to permute by the sodium ion mold by 1 mol/L-NaCl in the case of cation exchange membrane, and the quantum of the hydrogen ion which separated was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol). On the other hand, the chloride-ion mold was made to permute by the nitrate ion mold by 1 mol/L-NaNO<sub>3</sub> in the case of anion exchange membrane, and the quantum of the chloride ion which separated was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol).

[0040] Next, after being immersed in 1 mol/L-HCl for 4 hours or more and fully rinsing the same ion exchange membrane with ion exchange water, surface moisture was wiped off for the film with ejection tissue paper etc., and the weight at the time of humidity (Wg) was measured. Next, the film was put into the reduced-pressure-drying machine, and it was made to dry at 60 degrees C for 5 hours. The weight at the time of ejection desiccation (Dg) was measured for the film.

[0041] Ion exchange capacity and water content were computed by the degree type.

[0042] Ion exchange capacity =  $A \times 1000 / W$  [mmol/g-desiccation film]

Water content =  $100 \times (W - D) / D$  [%]

2) Water permeability JIS K The pure-water water permeability testing device based on 3821 was used. In 25 degrees C, the pure-water water permeability testing device was equipped with the ion exchange membrane used for measurement by the moisture state. Water permeability was searched for by the degree type.

[0043]  $C = Q25 / PC$ : Permeable [m<sup>3</sup>/h/100kPa]

The transparency flow rate of the water in Q25:25 degree C [m<sup>3</sup>/h]

P: Average film differential pressure [kPa]

3) In the transmission rate anion exchange membrane of an acid and alkali, the liquid which contains a 25-degree C 1 mol/L-sulfuric acid and 0.5 mol/L-magnesium sulfate in one room (undiluted solution room) was put in using the two-room cel made of acrylic resin divided by anion exchange membrane, and 25-degree C ion exchange water was put into one more room (dialysing fluid room). Both \*\* were stirred by the stirring child, the liquid of a dialysing fluid room was sampled after fixed time amount, the amount of transparency of a sulfuric acid was measured with potentiometric titration, and the amount of transparency of magnesium sulfate was measured with the atomic absorption spectro-photometer, respectively.

[0044] Moreover, in cation exchange membrane, in the above-mentioned approach, the liquid containing a 1 mol/L-sulfuric acid and 0.5 mol/L-magnesium sulfate was replaced with the liquid containing a 3 mol/L-sodium hydroxide and a 0.5 mol/L-aluminum hydroxide, same actuation was performed, and the amount of transparency of a sodium hydroxide and an aluminum hydroxide was measured. It asked for the transmission rate of each matter by the degree type.

[0045]  $U = A / (T - S \text{ and } **C)$

U: The transmission rate of an acid or alkali [mol/Hr-m<sup>2</sup>- (mol/L)]

A: An acid or the amount of transparency of alkali [mol]

T: Mixing time [Hr]

S: Effective film surface product [m<sup>2</sup>]

\*\*C: The acid of both \*\* before and behind stirring, or the logarithmic-mean concentration difference of alkali [mol/L]

According to the presentation table having shown in one to example 5 table 1, various monomers etc. were mixed and the monomer constituent was obtained. 400g of obtained monomer constituents was put into 500ml glassware, and the porous membrane made from polyethylene of weight average molecular weight 100,000 (A, B, C, D, every 20cmx 20cm) and the porous membrane made from polypropylene of weight average molecular weight 150,000 (E, 20cmx20cm) were immersed.

[0046] Next, glassware was made reduced pressure for 10 minutes to the pressure of 0.7kPa(s) with the vacuum pump, after carrying out reduced pressure deaeration, it returned to ordinary pressure and the hole of porous membrane was filled up with the monomer constituent. Then, after covering the both sides of porous membrane, having used ejection and 100-micrometer polyester film as exfoliation material for porous membrane out of the monomer constituent, the heating polymerization was carried out at 80 degrees C under the nitrogen application of pressure of 0.4MPa for 8 hours.

[0047] The obtained filmy material was immersed at 30 degrees C into the mixture of 1:4 of a methyl iodide and a methanol for 24 hours, and pyridinium mold anion exchange membrane was obtained.

[0048] The thickness of such pyridinium mold anion exchange membrane, ion exchange capacity, water content, water permeability, and a matter transmission rate were measured. These results were shown in a table 2.

[0049] Except having not performed reduced pressure deaeration actuation in example of comparison 1 example 1, the same actuation as an example 1 was performed and pyridinium mold anion exchange membrane was obtained.

[0050] The thickness of this pyridinium mold anion exchange membrane, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were measured. This result was shown in a table 2.

[0051] Thickness, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were similarly measured using the anion exchange membrane (commercial item A; Tokuyama make) marketed example of comparison 2. The result was shown in a table 2.

[0052] Example of comparison 3 polyethylene porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyethylene porous membrane was dried at ejection and 50 degrees C out of liquid. After repeating this actuation 5 times, reduced pressure drying was carried out at 80 degrees C for 2 hours, and the filmy material was obtained.

[0053] Methyl alcohol washed, after being immersed in the chloromethyl methyl ether which added 2% of the weight of anhydrous salt-ized tin and making the obtained filmy material react at 35 degrees C for 4 hours.

[0054] Next, the filmy material which chloromethylated was made to react to the mixed solution of 20:30:50 of a trimethylamine, an acetone, and ion exchange water at 30 degrees C 30% for 24 hours, and the anion exchange membrane which has a quaternary ammonium base as an ion exchange group was obtained.

[0055] The thickness of this anion exchange membrane, ion exchange capacity, water content, water permeability, and H<sub>2</sub>SO<sub>4</sub> transmission rate were measured. The result was shown in a table 2.

[0056] According to the presentation table having shown in six to example 10 table 1, the same impregnation as examples 1-5 and polymerization actuation were performed, the obtained filmy material was immersed for 45 minutes at 40 degrees C into the mixture of 1:1 of 98% concentrated sulfuric acid and the chlorosulfonic acid of 90% or more of purity, and sulfonic acid type cation exchange membrane was obtained.

[0057] The thickness of such sulfonic acid type cation exchange membrane, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were measured. These results were shown in a table 3.

[0058] Except having not performed reduced pressure deaeration actuation in example of comparison 4 example 6, the same actuation as an example 6 was performed and sulfonic acid type cation exchange membrane was obtained.

[0059] The thickness of this sulfonic acid type cation exchange membrane, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were measured. This result was shown in a table 3.

[0060] Thickness, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were similarly measured using the cation exchange membrane (commercial item B; Tokuyama make) marketed example of comparison 5. The result was shown in a table 3.

[0061] Example of comparison 6 polyethylene porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyethylene porous membrane was dried at ejection and 50 degrees C out of liquid. After repeating this actuation 5 times, reduced pressure drying was carried out at 80 degrees C for 2 hours, and the filmy material was obtained.

[0062] The obtained filmy material was immersed for 60 minutes at 40 degrees C into 98% concentrated sulfuric acid, and sulfonic acid type cation exchange membrane was obtained. The thickness of this sulfonic acid type cation exchange membrane, ion exchange capacity, water content, water permeability, and a NaOH transmission rate were measured. These results were shown in a table 3.

[0063]

[A table 1]

表1

| 実施例No. | 多孔質膜 <sup>1)</sup> | 組成(重量比)          |                    |                   |                    |                  |
|--------|--------------------|------------------|--------------------|-------------------|--------------------|------------------|
|        |                    | Si <sup>2)</sup> | 4-VP <sup>3)</sup> | DVB <sup>4)</sup> | ATBC <sup>5)</sup> | PO <sup>6)</sup> |
| 1      | A                  |                  | 80                 | 7                 | 5                  | 5                |
| 2      | B                  |                  | 80                 | 7                 | 5                  | 5                |
| 3      | C                  |                  | 80                 | 7                 | 5                  | 5                |
| 4      | D                  |                  | 80                 | 7                 | 5                  | 5                |
| 5      | E                  |                  | 80                 | 7                 | 5                  | 5                |
| 6      | A                  | 80               |                    | 7                 | 10                 | 5                |
| 7      | B                  | 80               |                    | 7                 | 10                 | 5                |
| 8      | C                  | 80               |                    | 7                 | 10                 | 5                |
| 9      | D                  | 80               |                    | 7                 | 10                 | 5                |
| 10     | E                  | 80               |                    | 7                 | 10                 | 5                |

1) 多孔質膜

A: ポリエチレン製、膜厚25 $\mu$ m、空隙率45%、平均孔径0.5 $\mu$ m

B: ポリエチレン製、膜厚50 $\mu$ m、空隙率60%、平均孔径0.5 $\mu$ m

C: ポリエチレン製、膜厚70 $\mu$ m、空隙率80%、平均孔径0.5 $\mu$ m

D: ポリエチレン製、膜厚100 $\mu$ m、空隙率80%、平均孔径0.5 $\mu$ m

E: ポリプロピレン製、膜厚50 $\mu$ m、空隙率70%、平均孔径0.2 $\mu$ m

2) スチレン

3) 4-ビニルピリジン

4) ジビニルベンゼン

5) アセチルクエン酸トリブチル

6) t-ブチルパーオキシエチルヘキサノエート

[0064]

[A table 2]

表2

| 実施例No. | 膜厚  | イオン<br>交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度                                   |                           |
|--------|-----|-------------|-----|----------------------|--|---------------------------|
|        |     |             |     |                      | H <sub>2</sub> SO <sub>4</sub><br>透過速度 | MgSO <sub>4</sub><br>透過速度 |
| 1      | 32  | 2.6         | 68  | 1.2                  | 26                                     | 0.091                     |
| 2      | 63  | 2.7         | 70  | 0.9                  | 22                                     | 0.083                     |
| 3      | 87  | 3.1         | 72  | 0.6                  | 18                                     | 0.076                     |
| 4      | 115 | 3.2         | 80  | 0.6                  | 15                                     | 0.066                     |
| 5      | 58  | 2.5         | 68  | 0.8                  | 20                                     | 0.078                     |
| 比較例1   | 30  | 1.6         | 55  | 29.2                 | 12                                     | 1.035                     |
| 比較例2   | 150 | 3.5         | 80  | 7.0                  | 6                                      | 0.101                     |
| 比較例3   | 29  | 0.2         | 30  | 82.4                 | 9                                      | 2.024                     |

膜厚[ $\mu$ m]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

H<sub>2</sub>SO<sub>4</sub>透過速度[mol $\cdot$ Hr<sup>-1</sup> $\cdot$ m<sup>-2</sup> $\cdot$ (mol $\cdot$ L)<sup>-1</sup>]

MgSO<sub>4</sub>透過速度[mol $\cdot$ Hr<sup>-1</sup> $\cdot$ m<sup>-2</sup> $\cdot$ (mol $\cdot$ L)<sup>-1</sup>]

透水性[m<sup>3</sup>/Hr/100kPa]

選択透過性[ - ]

[0065]

[A table 3]

表3

| 実施例No. | 膜厚  | イオン<br>交換容量 | 含水率 | 透水性<br>$\times 10^8$ | 透過速度         |                             |
|--------|-----|-------------|-----|----------------------|--------------|-----------------------------|
|        |     |             |     |                      | NaOH<br>透過速度 | Al(OH) <sub>3</sub><br>透過速度 |
| 6      | 35  | 2.7         | 59  | 1.3                  | 5.2          | 0.072                       |
| 7      | 62  | 2.6         | 58  | 0.8                  | 4.6          | 0.061                       |
| 8      | 88  | 3.0         | 69  | 0.6                  | 4.2          | 0.049                       |
| 9      | 114 | 3.1         | 72  | 0.4                  | 3.8          | 0.033                       |
| 10     | 59  | 2.6         | 62  | 0.8                  | 4.7          | 0.055                       |
| 比較例4   | 31  | 2.1         | 60  | 50.7                 | 3.3          | 0.986                       |
| 比較例5   | 180 | 2.5         | 51  | 8.8                  | 1.2          | 0.572                       |
| 比較例6   | 31  | 0.2         | 32  | 70.4                 | 3            | 0.802                       |

膜厚[ $\mu\text{m}$ ]

イオン交換容量[mmol/g-乾燥膜]

含水率[%]

NaOH透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]Al(OH)<sub>3</sub>透過速度[ $\text{mol}\cdot\text{Hr}^{-1}\cdot\text{m}^{-2}\cdot(\text{mol}\cdot\text{L})^{-1}$ ]透水性[ $\text{m}^3/\text{Hr}/100\text{kPa}$ ]

選択透過性[-]

[Translation done.]